

AD-A283 755



ON PAGE

1 AGENCY USE ONLY		2 REPORT DATE 1994		3 TYPE/DATES COVERED	
4 TITLE AND SUBTITLE ON THE FORMATION AND PROPERTIES OF A HIGH-TEMPERATURE RESIN FROM A BISPHTHALONITRILE				5 FUNDING NUMBERS	
6 AUTHOR P J BURCHILL					
7 FORMING ORG NAMES/ADDRESSES DEFENCE SCIENCE AND TECHNOLOGY ORGANIZATION, MATERIALS RESEARCH LABORATORY, PO BOX 50, ASCOT VALE VICTORIA 3032 AUSTRALIA				8 PERFORMING ORG. REPORT NO	
9 SPONSORING/MONITORING AGENCY NAMES AND ADDRESSES					
11 SUPPLEMENTARY NOTES					
12 DISTRIBUTION/AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A				128 DISTRIBUTION CODE	
13. ABSTRACT (MAX 200 WORDS): WHEN A 4,4'-BIS (3,4-DICYANOPHENOXY)BIPHENYL IS HEATED WITH SMALL AMOUNTS OF AROMATIC AMINE OR AMIDINE SALTS, A HIGHLY CROSSLINKED POLYTRIAZINE IS OBTAINED. THIS POLYMER HAS BEEN SHOWN TO BE THE SAME AS THAT REPORTED WHEN BISPHTHALONITRILES ARE HEATED WITH AMINES. SALTS PROMOTE THIS REACTION MORE READILY AND THE GLASS TRANSITION TEMPERATURE OF THE POLYMER AFTER POST-CURE IS 315° c IS GENERALLY 30° HIGHER THAN WHEN FREE BASES ARE USED. THE FRACTURE PROPERTIES AND ELASTICITY OF THE SALT-CURED POLYMER HAVE BEEN MEASURED AT TEMPERATURES UP TO 250°C. AS A MODEL SYSTEM, THE SELF REACTION OF PHTHALONITRILE PROMOTED BY AMINES AND THEIR SALTS HAS BEEN STUDIED. IN BOTH CASES, POLY (4-(2-CYANOPHENYL) - 1,3,5-TRIAZINE-2,6-DIYL-1,2-PHENYLENE) IS PRODUCED, AND MORE EFFICIENTLY USING THE SALTS. A REACTION MECHANISM FOR THIS POLYMERIZATION HAS BEEN PROPOSED.					
14 SUBJECT TERMS				15 NUMBER OF PAGES 7	
				16 PRICE CODE	
17 SECURITY CLASS.REPORT UNCLASSIFIED	18 SEC CLASS PAGE UNCLASSIFIED	19 SEC CLASS ABST. UNCLASS	20 LIMITATION OF ABSTRACT		

DTIC
ELECTE
AUG 26 1994
S G D

94-27224



94 8 25 064

On the Formation and Properties of a High-Temperature Resin from a Bisphthalonitrile

P. J. BURCHILL

DSTO, Materials Research Laboratory, PO Box 50, Ascot Vale, Victoria 3032, Australia

SYNOPSIS

When 4,4'-bis(3,4-dicyanophenoxy)biphenyl is heated with small amounts of aromatic amine or amidine salts, a highly crosslinked polytriazine is obtained. This polymer has been shown to be the same as that reported when bisphthalonitriles are heated with amines. Salts promote this reaction more readily and the glass transition temperature of the polymer after post-cure at 315°C is generally 30°C higher than when free bases are used. The fracture properties and elasticity of the salt-cured polymer have been measured at temperatures up to 250°C. As a model system, the self reaction of phthalonitrile promoted by amines and their salts has been studied. In both cases, poly[4-(2-cyanophenyl)-1,3,5-triazine-2,6-diyl-1,2-phenylene] is produced, and more efficiently using the salts. A reaction mechanism for this polymerization has been proposed. © 1994 John Wiley & Sons, Inc.

Keywords: bisphthalonitrile • cure catalysis • polymerization mechanism • polymer properties

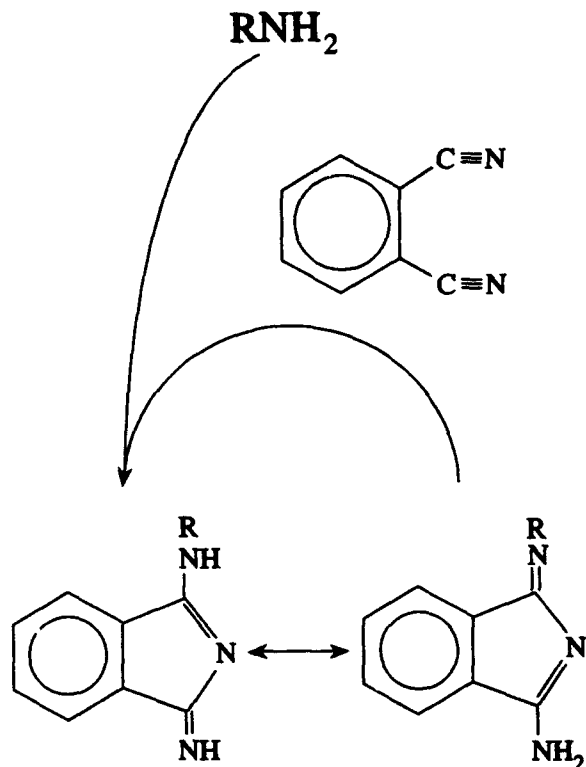
INTRODUCTION

Bisphthalonitriles were first considered as precursors for the synthesis of high temperature resistant polymers over 30 years ago by Marvell and Martin¹ when they attempted to produce a network of linked phthalocyanine units. Their monomer, bis(3,4-dicyanophenyl)ether, gave material which had only two or three linked units under their best conditions. Believing that this low reactivity was due to inflexibility in the monomer, many workers have synthesised and polymerized new monomers with chain lengths up to C₁₈ between the phthalonitrile ends.²⁻¹⁰ Such spacer groups as aliphatic di-amides and ethers, fluorinated hydrocarbon chains, and small polyphenyl ethers have been tried, and greater reaction appears to be evident. Finely divided transition metals or their salts were used to provide the necessary two electrons to form the phthalocyanine macrocycle. The polymers, however, were found to have poor resistance to heat in an oxidizing atmosphere due to metal-catalyzed oxidation. Wohrle and co-workers^{11,12} have thoroughly studied the formation of these poly(phthalocyanine)s using metals

and their salts and shown that high degrees of polymerization can be achieved. Organic reducing agents such as hydroquinone have been used to promote the reaction,¹³ but in this case they have the disadvantage that the large amount of co-reactant does not get incorporated into the polymer structure. This problem can be avoided by using a reducing agent which also contains a phthalonitrile group, as has been demonstrated by Pascal and co-workers¹⁴ who used 3,4-dicyanobenzhydrol in their polymerizations.

Much more stable polymers were obtained by heating the bisphthalonitrile monomers alone at 280°C for 6 days.¹⁵ Keller and Price¹⁶ then found that a reaction could be promoted by small amounts of primary amines at 240°C, and the reaction time with a post-cure at 315°C could be reduced to 48 h though this has not been optimized.¹⁷ This reaction (Scheme 1) was believed to give a polyisindolenine since phthalonitrile is known to react with ammonia and amines to yield aminoisindolenines.¹⁸⁻²¹ The aminoisindolenine group at the end of the chain was thought to be a reactive self-propagating chain end. It appeared that all that was necessary to promote polymerization was an active hydrogen source since phenols²² are also effective. Thus, the bisphthalonitriles were considered to react as difunc-

Accession For	
NTIS	CRA&I
DTIC	TAB
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	20



Scheme 1. Formation of a poly(isoindolenine).

tional monomers to yield a highly crosslinked poly(isoindolenine).

Because of the uncertainty regarding the structure of these polymers, phthalonitrile/aniline as a model system has been studied and compared with the amine promoted reaction of 4,4'-bis(3,4-dicyanophenoxy)biphenyl (BCPB). These investigations led to the use of amine and amidine salts to promote the reaction, and some mechanical properties of the amine salt-cured bisphthalonitrile are given.

RESULTS AND DISCUSSION

Model System

When phthalonitrile and aniline (20 : 1 w/w) were heated together in a sealed evacuated tube at 240°C for 24 h, three products were recovered. A trace of phthalocyanine is formed, a small amount of tris(2-cyanophenyl)-1,3,5-triazine (TCPT), and the remaining 60% was a yellow glassy material which,

unlike the triazine, is very soluble in common organic solvents such as benzene and acetone. The triazine was identified by its infrared and NMR spectra which have been published by Snow et al.¹³ The yellow glass gave an infrared spectrum very similar to that of TCPT with absorptions at 1520 and 1357 cm^{-1} due to the triazine ring, and a cyanide absorption at 2220 cm^{-1} . The ^{13}C -NMR spectrum of the glass confirmed the presence of a cyanide group at a different chemical shift to those in phthalonitrile. In addition, the resonances assigned to cyanide and the triazine ring for both the glass and TCPT had similar chemical shifts. The proton NMR spectrum of the glass also showed a strong downfield shift of an aromatic proton which has also been reported before for TCPT and assigned to the proton on the 2-cyanophenyl groups ortho to the triazine ring.¹³

Thin-layer chromatography of the yellow glass on silica gel showed that it was a mixture. This mixture was crudely fractionated by column chromatography on silica gel and the infrared spectra of all fractions were found to be very similar. Slight differences in the relative intensities of the cyanide and triazine absorptions were observed as the chromatographic mobility of the components decreased. Chromatographic analyses also showed that the infrared absorptions due to cyanide and triazine groups of the glassy material obtained from these model reaction studies were not due to dissolved TCPT or unreacted phthalonitrile, so confirming the ^{13}C -NMR analysis. Thus, it appears that the major product is a mixture of oligomers with the most likely structure being that shown in Figure 1, poly[4-(2-cyanophenyl)-1,3,5-triazine-2,6-diyl-1,2-phenylene]. Polymerization is proposed to take place through the 2-cyanophenyl substituents of the initially formed triazine also reacting with phthalonitrile.

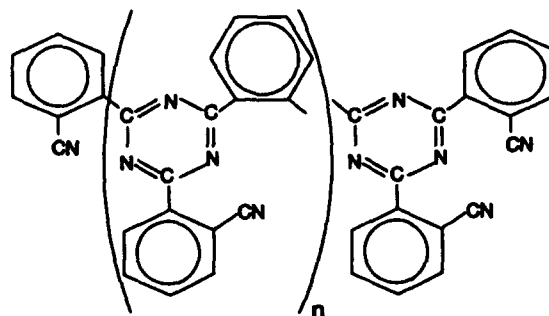


Figure 1. Poly[4-(2-cyanophenyl)-1,3,5-triazine 2,6-diyl 1,2-phenylene].

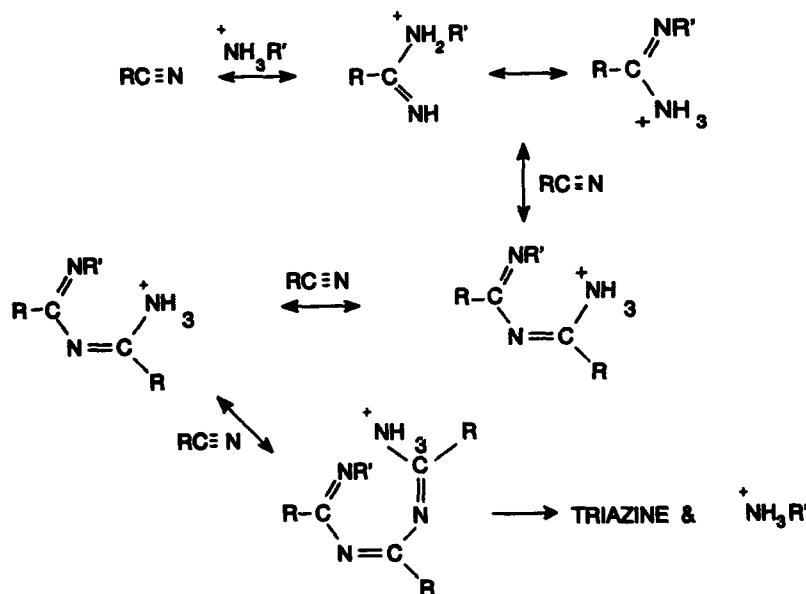
Reaction with Amine Salts

Generally organic cyano compounds do not react with amines unless the cyano group is activated by electron-withdrawing groups; in this case an amidine is formed.²³ Acids may also activate the cyano group towards nucleophilic attack by an amine.²⁴ Oxley and Short²⁵ showed that amidines could be easily obtained from aromatic cyanides by heating them with an excess of an aromatic primary amine salt. Similarly, the amidine group as part of a nitrogen heterocycle is produced in the intramolecular cyclization of ω -amino-1-cyanoalkanes when heated as their hydrochlorides.²⁶

When phthalonitrile was heated with the salt, aniline *p*-toluenesulfonate, under the conditions described in the previous section, the same reaction products were recovered. A reaction route (discussed in more detail later) for polymerization and formation of triazine rings is shown in Scheme 2 in which an amidine salt chain end is the propagating species. The same scheme without the ions applies to the reactions using free bases. Cyclization to produce triazine eliminates the initial salt which is freed to initiate a new reaction sequence. Polymerization is through the 2-cyanophenyl substituents on the initially formed triazine. The same products were obtained using benzamidine hydrochloride and *N*-phenylbenzamidine *p*-toluenesulfonate to initiate the reaction. The yield of TCPT when salts were used was about half that produced with the free bases which is probably due to the 2-cyano groups reacting much more readily with the salt.

Polymerization of 4,4'-Bis(3,4-dicyanophenoxy)biphenyl

During cure of this monomer using 1,3-bis(3-aminophenoxy)benzene (APB) as initiator infrared spectra show the development of new absorptions at 1520 and 1357 cm^{-1} due to triazine, and a decrease in the nitrile absorption at 2230 cm^{-1} with a shift to 2220 cm^{-1} . This decrease in intensity of the nitrile absorption relative to an absorption at 1008 cm^{-1} is shown in Figure 2. Even after cure at 240°C for 24 h and post-cure at 315°C for 24 h, the nitrile absorption is about 30% of its original intensity. Figure 3 shows the infrared spectrum of the post-cured polymer. The effect of post-cure was an increase in the intensity of the absorptions ascribed to triazine and a decrease in the nitrile absorption. Assuming no changes in the extinction coefficients, one-third of the cyanide groups remain unreacted which is what would be expected if polymer with the general structure given in Figure 1 is formed. Further reaction of these cyanide groups to give triazine appears to be unlikely due to steric hindrance. Evidence of the formation of triazines during the early stages of reaction was found by spectral subtraction. To obtain this a spectrum of the glassy form of the monomer was required (Fig. 4) since cooled reaction mixtures were glasses. The difference spectra showed no additional peaks other than those assigned to triazine, and thus showed that the initial product was spectrally the same as the product after post-cure. Thus these triazines are also formed in the earliest stages of the reaction.



Scheme 2. Formation of a triazine.

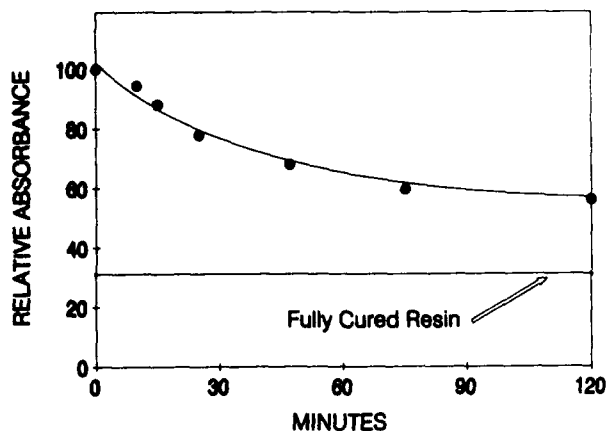


Figure 2. Change in the intensity of the nitrile absorption relative to the adsorption at 1008 cm^{-1} during cure at 240°C .

When an amine salt is used the same polymer as indicated by its infrared spectrum is produced in much shorter time. Figure 5 gives the glass transition temperature change with reaction time for amine and amine salt promoted reactions. The molar concentration of amine was $\frac{1}{40}$ that of the monomer, while the salt was at $\frac{1}{100}$ of monomer in these experiments. Post-cure at 315°C raised the glass transition temperature of these polymeric products to 245 and 290°C , respectively. The reaction is just as effectively promoted using an amidine salt such as *N*-phenylbenzamidine *p*-toluenesulfonate, and Table I gives the final glass transition temperatures of several amine and amine salt promoted reaction products. The polymerization appears to go further towards completion using a salt. In all cases the polymers formed are intensely green which is most likely due to the formation of phthalocyanines from traces of impurities acting as reducing agents.

A differential scanning calorimetry study of the APB-catalyzed reaction revealed a weak exotherm

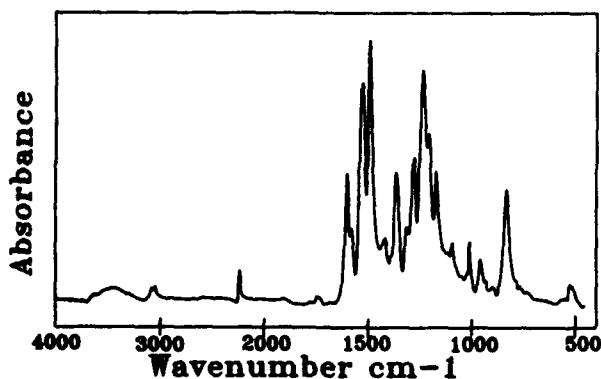


Figure 3. Infrared spectrum of the post-cured resin.

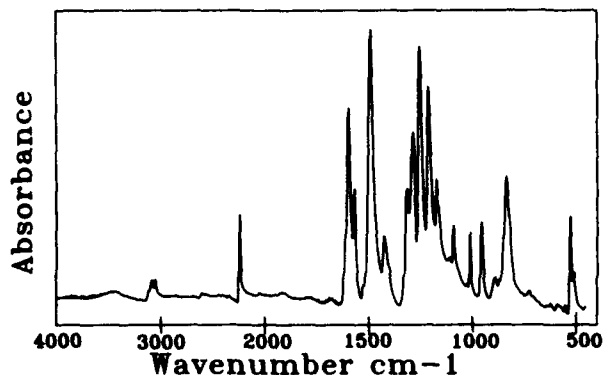


Figure 4. Infrared spectrum of the glassy form of 4,4'-bis(3,4-dicyanophenoxy)biphenyl.

above 250°C . Analysis of the exotherm peak position at various scanning rates gave an activation energy of 82 kJ mol^{-1} . A similar study using phthalonitrile with APB showed a similar exotherm and an activation energy of 78 kJ mol^{-1} was obtained. The first trimerization step is felt to be responsible for this exotherm, and that this triazine reacts more slowly to produce the polymer.

Mechanical Properties

Some of the mechanical properties of resins from amine and phenol promoted cure of bisphthalonitriles have been reported before.^{22,27} A study has been made of the amine salt-cured material and the results are given in Table II. The room temperature values are similar to those reported before for amine-cured material. The brittle fracture toughness is lower at 200°C as expected due to the decrease in modulus. At 250°C the double torsion fracture test used shows stick-slip behavior which indicates the

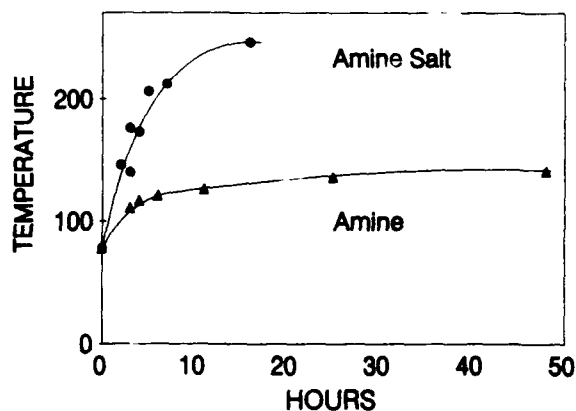


Figure 5. The glass transition temperature change with reaction time for amine and amine salt promoted reactions.

Table I. Cure of 4,4'-Bis(3,4-Dicyanophenoxy)biphenyl: Variation of Glass Transition Temperature with Curing Agent^a

Curing Agent	Glass Transition Temperature (°C)
1,3-Bis(3-aminophenoxy)benzene	256
1,3-Bis(3-aminophenoxy)benzene <i>p</i> -toluenesulfonate	302
<i>p</i> -Phenylenediamine <i>p</i> -toluenesulfonate	294
Bis(4-aminophenyl)methane	263
Bis(4-aminophenyl)methane hydrochloride	289
Toluenesulfonic acid monohydrate	295
2,2-Bis(4-hydroxyphenyl)propane	173

^a Cure conditions: 16–24 h at 240°C and 7–24 hours at 315°C.

material is becoming more ductile as its glass transition temperature is approached, and the critical stress intensity factor (K_{IC}) and strain energy release rate (G_{IC}) values increase. This resin would appear to be suitable for use at temperatures up to at least 250°C which could probably be raised further by post-curing at higher temperatures in an inert atmosphere since it has already been shown that such treatment will increase the glass transition temperature of bisphthalonitrile polymers.²⁸

Reaction Mechanism

The polymerization of the bisphthalonitrile appears to be similar to the model system and results in extensive triazine ring formation. Keller²⁸ had also proposed the existence of triazine structures in the polymer on the grounds that there are residual cyano groups even after post-cure at 500°C. Amines had been proposed to react with the cyano groups and with concurrent cyclization a 3-amino-1-imino-isoindolenine (AII) produced. The AII was then considered to react with another phthalonitrile group to give chain extension and regeneration of the aminoisoindoleine end. Reports of formation of

isoindolenines from phthalonitrile indicate that a catalyst is required,²⁰ the amine is present in greater than stoichiometric amounts, and the products recovered are *N,N'*-disubstituted AIIs and ammonia. Isoindolenines were also reported in the reactions of phthalonitrile and pyromellitonitrile when stoichiometric amounts of diamines were used to give polymers and macrocycles.²⁹

An alternative route to the formation of AII from phthalonitriles could be reaction of both cyanide groups to give a bisamidine which cyclizes very rapidly with elimination of ammonia. However there has been no report of isolation or formation of an amidine from a phthalonitrile. At very low concentrations of amine the chance of both cyanide groups reacting is minimal and so isoindolenine formation by this route is unlikely. The evidence suggests that the mono-amidine reacts more readily with a nitrile on another phthalonitrile group than intramolecularly which would not be unreasonable since an amidine group would deactivate an adjacent cyano group. Oxley and Short's work²⁵ shows that these types of reaction occur more readily if there are electron-withdrawing substituents on the benzene ring to activate the cyanide group. After reaction of three phthalonitrile groups cyclization occurs to give a triazine as shown in the Scheme 2. Formation of triazines from aromatic nitriles is well known,^{30–33} and this reaction is catalyzed by toluenesulfonic acid,³⁴ in this work Hsu showed that high yields of the triazine can be obtained with activated nitriles such as *p*-cyanobenzoic acid.

In the proposed Scheme 2, the formation of the amidine groups occurs via initial protonation of the cyano group nitrogen followed by nucleophilic attack by free base at the carbon. The greater degree of polymerization using salts would be due to the easier reaction of the 2-cyanophenyl groups through pro-

Table II. Mechanical Properties of Phthalonitrile Resin Produced Using *p*-Phenylenediamine *p*-Toluenesulfonate

Property	Temperature		
	24°C	200°C	250°C
$K, \text{MN m}^{-3/2}$	0.82	0.65	0.82
$G, \text{J m}^{-2}$	164	127	236
E, GPa	4.1	3.3	2.9

tonation and reaction with base than with base alone. Acid-catalyzed trimerization suggests that protonated cyano groups may also undergo nucleophilic attack by other cyano groups even though these are very weak bases. However, in the typical reaction conditions with acids small amounts of water initially present could provide the necessary base from hydrolysis of the cyano group.

Scheme 2 is supported by production of triazines when an amine salt is used with other aromatic nitriles. With benzonitrile heated to 250°C with 5% of aniline *p*-toluenesulfonate a 4% yield of 2,4,6-triphenyl-1,3,5-triazine is obtained after 10 days. Similarly when isophthalonitrile was heated for a week at 250°C with the aniline salt a 25% yield of a crystalline triazine melting at 376°C was obtained. Also recovered were about 20% of the initial weight of isophthalonitrile as soluble triazine oligomers and the remaining material was unreacted isophthalonitrile. The crystalline triazine is most likely to be tris(3-cyanophenyl)-1,3,5-triazine, and its infrared spectrum is given in Figure 6 showing the triazine absorptions at 1528 cm^{-1} and the usual 1360 cm^{-1} peak as a doublet at 1368 and 1350 cm^{-1} . The difference in behavior of isophthalonitrile is due to the meta cyano groups not being as activated towards nucleophilic attack as ortho cyano groups, and similarly in the triazine product the meta cyano group is not as activated by the electron deficient triazine ring as an ortho cyano group would be.

SUMMARY

Bisphthalonitriles when heated with small amounts of reactive hydrogen sources, such as amines, amidines and their salts, and phenols polymerize to yield

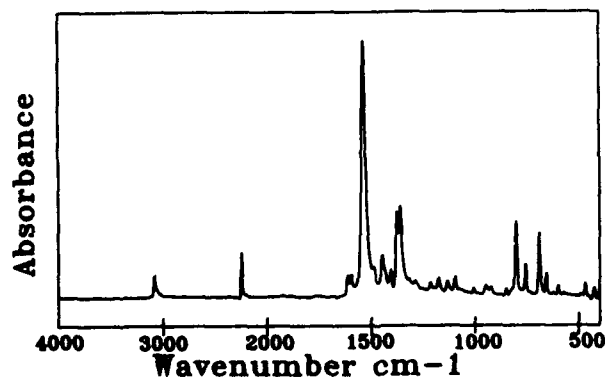


Figure 6. Infrared spectrum of the crystalline product from the self condensation reaction of 1,3-dicyanobenzene: tris(3-cyanophenyl)-1,3,5-triazine.

a network of linked triazine rings. Model systems suggest that after the first involvement of a phthalonitrile group in triazine formation, the residual cyano groups also react and in this way a high crosslink density is acquired and so a high glass transition temperature. This second stage of the reaction is more efficiently promoted with amine salts because of the reduced reactivity of the cyano groups. These reactions are most likely to be acid catalysis of the nucleophilic addition of a base to a cyano group.

EXPERIMENTAL

Materials

Bis(3,4-dicyanophenoxy)-4,4'-biphenyl was obtained from the Eastman Kodak Co. *N*-phenylbenzamidinium was obtained by the method given by Rabjohn from the reaction of aniline with benzonitrile.³⁵ *p*-Toluenesulfonate salts were prepared by slow addition of stoichiometric methanol or isopropanol solutions of the amine or amidine to a similar solution of the acid. The precipitated product was collected, washed with solvent, and dried. Hydrochlorides were prepared by passing hydrogen chloride gas into a solution of the base.

Amine and Amine Salt Catalyzed Reactions of Nitriles

Recrystallized and dried phthalonitrile (1 g) and aniline (0.05 g) were placed in a glass tube which was quickly evacuated and sealed and then placed into an air-circulating oven at 250°C. The initially pale yellow liquid turned green during the first hour, and after 2–3 h a solid began to separate. After 24 h the tube was broken and the mixture extracted in a hot soxhlet with benzene. After extraction all that remained in the extraction thimble was a small amount (20 mg) of a dark blue compound—a phthalocyanine. The yellow benzene solution was evaporated to dryness and the product heated with a small amount of methylene chloride. The insoluble portion was collected and identified by its infrared spectrum¹³ as tris(2-cyanophenyl)-1,3,5-triazine (TCPT), yield ~ 400 mg. The soluble fraction was analyzed by thin-layer chromatography on silica gel using benzene/acetone (10 : 1 v/v) as eluent. Further fractionation was achieved by column chromatography on silica gel (Merck Kieselgel 60) using benzene and benzene/acetone mixtures. Similar reactions were performed using aniline *p*-toluenesulfonate, *p*-phenylene diamine *p*-toluenesulfonate, benzamidinium hydrochloride, *N*-phenylbenzamidinium,

and its *p*-toluenesulfonate salt as catalysts and the yields of TCPT were about 200 mg. Other nitriles used were benzonitrile and 1,3-dicyanobenzene and triazines were recovered and identified.

Polymerization of Bis(3,4-dicyanophenoxy)-4,4'-biphenyl (BCPB)

To obtain void free specimens for double torsion testing, BCPB (Eastman Kodak Co.) was heated in vacuum at 240°C for 4 h to remove residual solvents and moisture. To the molten monomer at 260°C was added catalyst (0.5–1.5 wt %) and the mixture stirred for 15 min before being poured into a heated mold. The filled mold was degassed in a vacuum oven at 220°C for 15 min, and then placed in an air-circulating oven. After 16 h at 240°C, the oven temperature was raised to 315°C for a further 7 h when a salt was used as a catalyst. With other catalysts the cure schedule was 24 h at 240°C and 24 h at 315°C.

For other polymerizations initial degassing of the monomer was not necessary because the quantities involved were much smaller. The monomer was melted catalyst added and dissolved then the mixture cooled rapidly to give a friable glass which was broken up and placed into small sample containers for monitoring the cure process by withdrawal. Glass transition temperatures were measured by DSC during the early stages of the cure and by TMA at later stages.

Mechanical Properties

Toughness of cast plates of poly(BCPB) was measured using the double torsion method.^{36,37} The strain energy release rate (G_{IC}) was determined from the force (P) required to propagate the crack and the compliance (C) calibration of the specimen using:

$$G_{IC} = P^2 / 2t_n \cdot dC/da$$

where a is the crack length and t_n is the plate thickness at the groove. The critical stress intensity factor (K_{IC}) was calculated from:

$$K_{IC}^2 = (1 + \nu) \cdot P^2 L^2 / W t_n^3 k_1$$

in which t is the plate thickness, W is the plate width, L is length of the moment arm for the applied load P , ν is Poissons ratio, and k_1 a factor to correct for

finite thickness to width ratios.³⁸ The material modulus (E) was calculated from the relationship

$$K^2 = GE$$

The author acknowledges the opportunity to do this work while on secondment to the Naval Research Laboratory, Washington DC, and is thankful for the support given by W. Moniz, T. Keller, and A. Snow through their interest in the project, and for the assistance of Antonietta Giglio.

REFERENCES AND NOTES

1. C. S. Marvel and M. M. Martin, *J. Am. Chem. Soc.*, **80**, 6600 (1958).
2. J. R. Griffith and T. R. Walton, *ACS Polym. Prepr.*, **15**(1), 787 (1974).
3. T. R. Walton, J. R. Griffith, and J. G. O'Rear, *Org. Coating & Plast. Prepr.*, **34**(2), 446 (1974).
4. J. R. Griffith, J. G. O'Rear, and T. R. Walton, *Adv. Chem. Ser.*, **142**, 458 (1975).
5. T. M. Keller and J. R. Griffith, *Org. Coatings Plast. Prepr.*, **39**, 546 (1978).
6. T. M. Keller and J. R. Griffith, *ACS Symp. Ser.*, **132**, 25 (1980).
7. T. M. Keller, T. R. Price, and J. R. Griffith, *Synthesis*, 613 (1980).
8. T. R. Walton, J. R. Griffith, and J. P. Reardon, *J. Appl. Polym. Sci.*, **30**, 2921 (1985).
9. B. N. Achar, G. M. Fohlen, and J. A. Parker, *J. Appl. Polym. Sci.*, **29**, 353 (1984).
10. D. Woehrle and B. Schulte, *Makromol. Chem.*, **189**, 1229 (1988).
11. D. Woehrle and B. Schulte, *Makromol. Chem.*, **189**, 1167 (1988).
12. G. Knothe and D. Woehrle, *Makromol. Chem.*, **190**, 1573 (1989).
13. A. W. Snow, J. R. Griffith, and N. P. Marullo, *Macromolecules*, **17**, 1614 (1984).
14. T. Pascal, J. Malinge, and B. Sillion, *J. Polym. Sci. Part A: Polym. Chem.*, **27**, 2777 (1989).
15. T. M. Keller, T. R. Price, and J. R. Griffith, *Org. Coat. Plast. Chem.*, **43**, 804 (1980).
16. T. M. Keller and T. R. Price, *J. Macromol. Sci. Chem.*, **A18**, 931 (1982).
17. T. M. Keller, private communication.
18. J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 5000 (1952).
19. P. F. Clark, J. A. Elvidge, and R. P. Linstead, *J. Chem. Soc.*, 3593 (1953).
20. W. O. Siegl, *J. Org. Chem.*, **42**, 1872 (1977).
21. S. A. Siling, I. I. Ponomarev, V. V. Kuznetsov, B. V. Lokshin, V. V. Korshak, and S. V. Vinogradova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1755 (1983).
22. T. M. Keller, US Pats. 4,408,035 and 4,410,676 (1983).
23. F. C. Schaefer, in *Chemistry of the Cyano Group*, Z.

- Rappoport, Ed., Interscience, New York, 1970, chapter 6.
24. A. I. Meyers and J. C. Sircar, in *Chemistry of the Cyano Group*, Z. Rappoport, Ed., Interscience, New York, 1970, chapter 8.
 25. P. Oxley and W. F. Short, *J. Chem. Soc.*, 147 (1946).
 26. F. F. Blick, A. J. Zambito, and R. E. Stenseth, *J. Org. Chem.*, **26**, 1286 (1961).
 27. R. Y. Ting, T. M. Keller, T. R. Price, and C. F. Poranski, *ACS Symp. Ser.*, **195**, 337 (1982).
 28. T. M. Keller, *J. Polym. Sci. Part A: Polym. Chem.*, **26**, 3199 (1988).
 29. D. I. Packham, *Br. Polym. J.*, **2**, 280 (1970).
 30. A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 273 (1941).
 31. C. Grundmann, G. Weisse, and S. Seide, *Ann.*, **577**, 77 (1952).
 32. T. L. Cairns, A. W. Larchar, and B. C. McKusick, *J. Am. Chem. Soc.*, **74**, 5633 (1952).
 33. S. D. Ross and M. Fineman, *J. Am. Chem. Soc.*, **72**, 3302 (1950).
 34. Li-Chen Hsu, *ACS Symp. Ser.*, **4**, 145 (1972).
 35. N. Rabjohn, *Organic Syntheses Collected Volume IV*, Wiley, New York, 1963, p. 769.
 36. J. A. Kies and B. J. Clark, in *Fracture 1969*, P. L. Pratt, Ed., Chapman & Hall, London, 1969, p. 483.
 37. G. P. Marshall, L. H. Coutts, and J. G. Williams, *J. Mater. Sci.*, **9**, 1409 (1974).
 38. S. P. Timoshenko and J. N. Goodier, *Theory of Elasticity*, McGraw-Hill, London, 1982, chapter 10.

Received May 26, 1992

Accepted May 18, 1993